CAHIERS MAGELLANES-NS
Volume 06 Issue 2
2024

ISSN:1624-1940
DOI 10.6084/m9.figshare.26075233
http://magellanes.com/

Selective and Efficient Liquid Phase Oxidation of Benzyl Alcohol to Benzaldehyde by *Tert*-Butyl Hydrogen Peroxide over Al_2O_3-ZrO_2 Mixed Oxide Catalyst

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Abstract: A binary metal oxide Al_2O_3-ZrO_2 (1:1) material catalyzed efficiently the solventless oxidation of benzyl alcohol (BOL) by *tert*-butyl hydrogen peroxide (TBHP) and produced selectively the benzaldehyde (BAL) in high yields. The mixed oxide of Al_2O_3-ZrO_2 (1:1) catalyst was prepared via an ultra-diluted co-precipitation method and characterized by XRD, N_2 adsorption-desorption, NH_3-TPD and CO_2-TPD, SEM and XPS techniques. The Al_2O_3-ZrO_2 (1:1) mixed oxide catalyst showed a higher conversion (71%) of benzyl alcohol and selectivity towards the benzaldehyde (85%) product in comparison to that of individual metal oxide catalysts i.e. Al_2O_3 and ZrO_2. The influence of reaction parameters like temperature, reaction time and catalyst loading were studied to optimize the catalytic conditions. Catalyst recovery and reusability experiments revealed that the above binary metal oxide is stable up to five catalytic cycles. The optimized catalytic oxidation conditions were extended to study the substrate scope and a total of eight different BAL products were efficiency synthesized.

Keywords: Benzylalcohol, Benzaldehyde, TBHP, Mixed metal oxides, Oxidation catalysts.

1. INTRODUCTION

The selective oxidation of aromatic alcohols to the aldehydes is an imperative reaction in basic research and industrial processes [1–3]. Among the aldehydes, benzaldehyde (BAL) is a versatile intermediate and high-valuable chemical widely used in the pharmaceutical, dyestuff, food, cosmetic, and agrochemical industries [4–7] more over the oxidation of benzyl alcohol to benzaldehyde is practically important reaction for the production of chlorine-free benzaldehyde required in perfumery and pharmaceutical industries.Liquid phase oxidation of benzyl alcohol is an important preferred reaction practically for the production of chlorine-free benzaldehyde, without loss of carbon in the form of CO_2 (a greenhouse gas) [8,9].

Traditionally, oxidation of alcohols has been performed with a stoichiometric amount of metal oxidants, such as Cr(VI) salts, permanganate and bromate reagents. However, these reagents show poor atom efficiency and generate a large amount of environmentally ill-disposed heavy-metal waste.Therefore, catalytic oxidation methods, which employ a variety of transition metals such as Cu(I), Ni(II), Co(II), Pd(II) and manganese oxides using molecular oxygen, H_2O_2 and TBHP as oxidizing agents are well explored[10-16].The catalytic oxidation of BOL has also been performed in various organic solvents, including dimethyl sulfoxide (DMSO), toluene, diethoxyethane, benzene, dimethyl formamide (DMF), chloroform, etc. These procedures produce more unwanted organic waste, and the solvents and oxidants raise severe environmental issues, which motivates emerging alternative catalytic oxidation processes [17-22]. Thus, most researchers have focused on inexpensive and non-toxic reagents adhering to "green chemistry" principles [19].

Numerous efforts on developing efficient catalysts towards these oxidations have been progressed and reported. Solvent-free approach is an attractive green process for selective oxidation of benzyl alcohol and oxidants like molecular oxygen, hydrogen peroxide (H_2O_2) and TBHP are in the order as green options.Nevertheless, the cost, preparation method, thermal stability of the catalyst, solvent for oxidation, use of the external base, andnature of the active sites of catalyst are the important concerns in promoting a suitable heterogeneous catalyst for selective oxidations[23–31].

Binary metal oxides (BMOs) are a class of heterogeneous catalysts, easy to synthesize, exhibits good thermal stability, and are found to exhibit good productivity and selectivity for the catalytic oxidation of alcohols including BAL. BMOs can be obtained easily from different types of metallic combinations, via different preparation methods, viz., co-precipitation, wet impregnation, sol-gel, and solid-state mixing. A variation in the catalyst preparation method may provide different physicochemical properties and diversity in active sites that would be beneficial for intended catalysis [32-34]. Furthermore, BMOs can exhibit appreciable synergistic effects during catalytic transformation.

As a follow-up to the previous work, we planned to study the solvent-free oxidation of BAL to BOL using tert-butyl butyl hydrogen peroxide (TBHP) as oxidant over a very effective and low cast Al_2O_3-ZrO_2 (1:1) Binary Mixed Metal oxide (BMO).The highly efficient Al_2O_3-ZrO_2 catalyst and individual oxides synthesized by a simple co-precipitation method, characterised by various techniques. The catalyst used to study the oxidation of BAL and optimized reaction conditions like temperature, time and catalyst weight. We also studied the substrate scope application.

2. EXPERIMENTAL SECTION

2.1 Materials and Chemicals

In order to prepare the examined catalysts, a variety of chemicals were purchased from commercial vendors, namely, $Al(NO_3)_3{\cdot}9H_2O$ (Analytical grade, S.D fine Chemicals), $ZrO(NO_3)_2$(Analytical grade, Avra chemicals), NH_3solution (Analytical grade, S.D fine Chemicals) used were of laboratory grade, Aromatic alcohols, TBHP (Analytical grade, Sigma Aldrich), India and we used without further purification.

2.2 Catalysts preparation

The highly efficient mixed oxide of Al_2O_3-ZrO_2 (1:1) catalyst was prepared via an ultra-diluted co-precipitation method (Figure 1). Initially, the appropriate amounts of $Al(NO_3)_3{\cdot}9H_2O$ and $ZrO(NO_3)_2$ precursors were dissolved in a minimal volume of water, then diluted up to 1000 mL with deionized water and stirred for 30 minutes. Subsequently, a 15% NH_3 solution was added drop wise with continuous stirring until the pH reached 9. The stirring was continued for 24 hours, followed by aging at room temperature for an additional 24 hours. The resulting mixture was then filtered and washed with deionized water until reaching a neutral pH of 7. The obtained product was dried overnight at 110°C and calcined at 500 °C for 5 hours under atmospheric air.

ISSN:1624-1940
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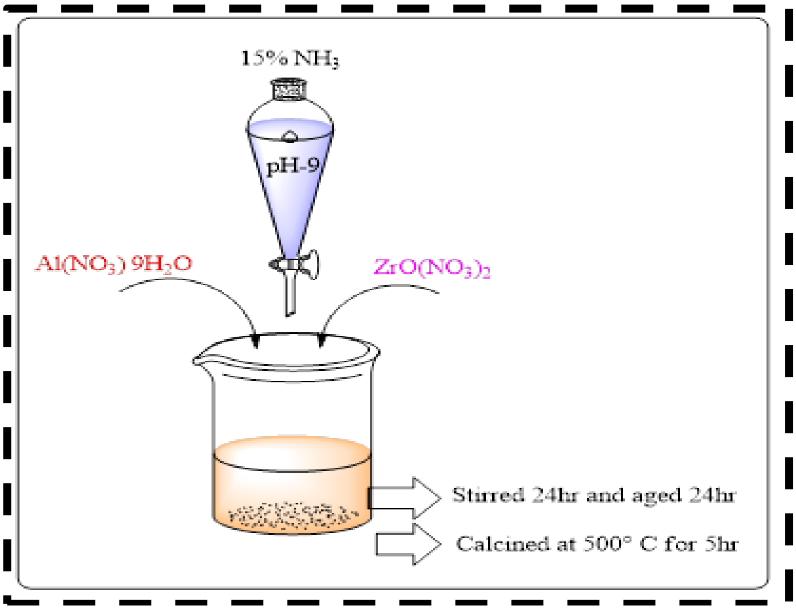

Figure 1: Preparation of Al-Zr catalyst.

3. RESULTS AND DISCUSSION

3.1 Catalyst Characterization

Figure 1 displays the X-ray diffraction (XRD) patterns for the mixed oxides Al_2O_3-ZrO_2 (1:1) after they were heated to 500°C (Figure 2). The spectrum shows distinctive γ-Alumina peaks when compared to pure Al_2O_3 and ZrO_2 from earlier findings, suggesting that the synthesised alumina is mostly amorphous. Additionally, minor peaks at 2θ angles of 46˚ and 66° are seen. The ZrO_2 XRD pattern often exhibits strong peaks at around 30°, 35°, 50°, 60°, 62°, and 74°, which are indicative of the tetragonal-ZrO_2 phase [PCPDF-06-6787]. Peaks related to Al_2O_3 are discernible in the mixed oxide catalysts, whereas ZrO_2 peaks are not, perhaps because the sizes of the Al^{3+} and Zr^{4+} ions are identical. There are also no peaks showing that Zr has been incorporated into the Al lattice, forming an Al_2O_3-ZrO_2 solid solution.

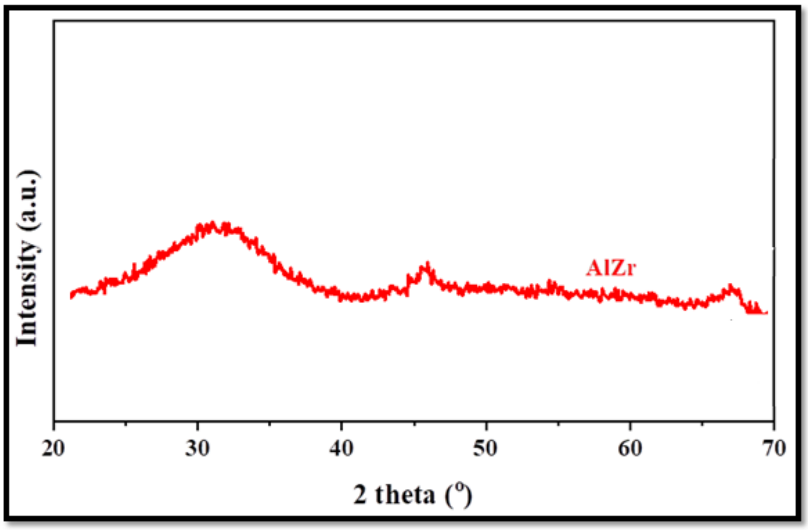

Figure 2: XRD patterns of all the synthesized Al_2O_3-ZrO_2 (AlZr)catalyst.

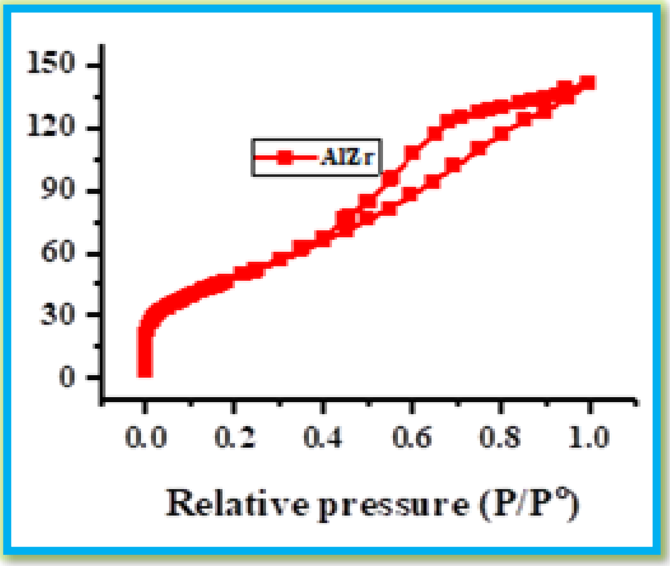

Figure 3: N_2-adsorption-desorption isotherms of the synthesized Al_2O_3-ZrO_2 (Al-Zr) catalyst.

Figure 3 depicts the N_2 adsorption and desorption isotherms for all synthesized catalysts. These isotherms show type-IV patterns with H_2-type hysteresis loops, which indicate the existence of mesopores. Table 1 shows the detailed textural features of the catalysts. Al_2O_3 surface area was measured at 268.5m²/g, whereas ZrO_2 surface area was 83.3m²/g. The Al_2O_3-ZrO_2 solid solution has a significantly enhanced surface area of 273.6 m²/g. This rise indicates increased surface activity as a result of ZrO_2 incorporation into the Al_2O_3 lattice. Because of its porous nature, Al_2O_3 has a greater surface area and hence more adsorption sites. However, the inclusion of ZrO_2, which also has a large surface area, contributes to an increase in active sites, hence improving catalytic activity.

A higher surface area often correlates with greater catalytic activity, as it exposes more active sites for reactions (Table 1). Moreover, pore size distribution is crucial in catalysis. The Al-Z rnanocatalyst demonstrated well-defined pore structures and suitable pore sizes, facilitating reactant diffusion and product desorption, ultimately leading to improved catalytic performance.

Table 1: Physicochemical features of the catalysts

Catalyst	**$S_{BET}(m^2/g)^a$**	**PV $(cm^3/g)^b$**	**PS $(nm)^b$**
Al_2O_3-ZrO_2	281.6	0.213	6.10

^{a}from BET analysis; ^{b}from N_2 adsorption desorption analysis; PV : pore volume; PS : pore size.

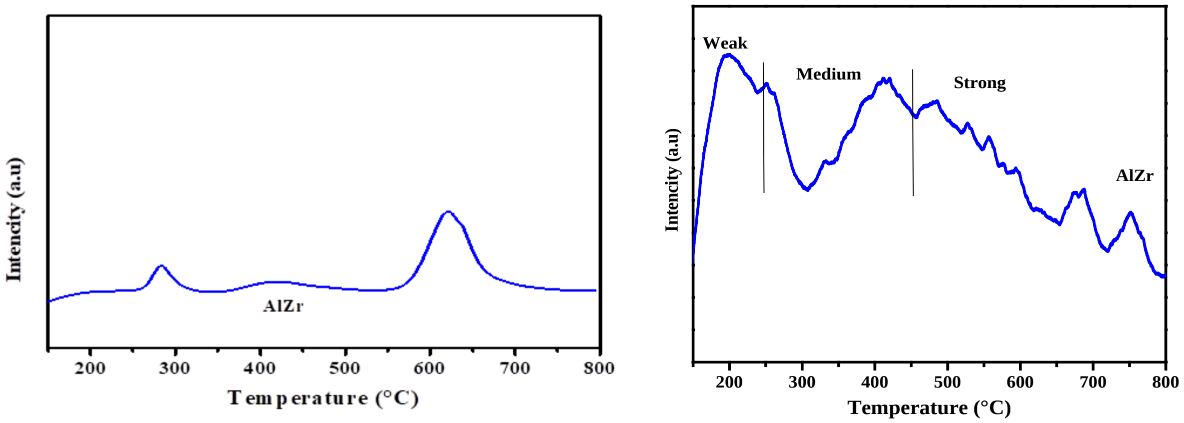

Figure 4: NH_3-TPD and CO_2-TPD of the synthesized Al_2O_3-ZrO_2 (AlZr) catalyst.

ISSN:1624-1940
DOI 10.6084/m9.figshare.26075233
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The NH_3 –TPD profiles of the synthesized catalysts were depicted in Figure 4. Acid site distribution generally falls into three categories: weak (<250 °C), medium (250-400 °C), and strong (>400 °C). The Al catalyst exhibited primarily weak acid sites, whereas the Zr catalyst displayed medium and strong acid sites. Interestingly, the AlZr mixed oxide catalyst showed predominantly strong acidic sites, with no presence of weak or medium sites.Additionally, CO_2-TPD of the AlZr mixed oxide catalyst was conducted to assess its basicity in figure 4. Similar to NH_3-TPD, basic sites were classified as weak (<250 °C), medium (250-400 °C), and strong (>400 °C). The AlZr catalyst exhibited all three types of basic sites.The TPD results suggest that the synthesized samples contain both acid and base pairs, likely contributing to the excellent yield of Knoevenagel condensation product, which typically requires acid-base pairs for catalysis.

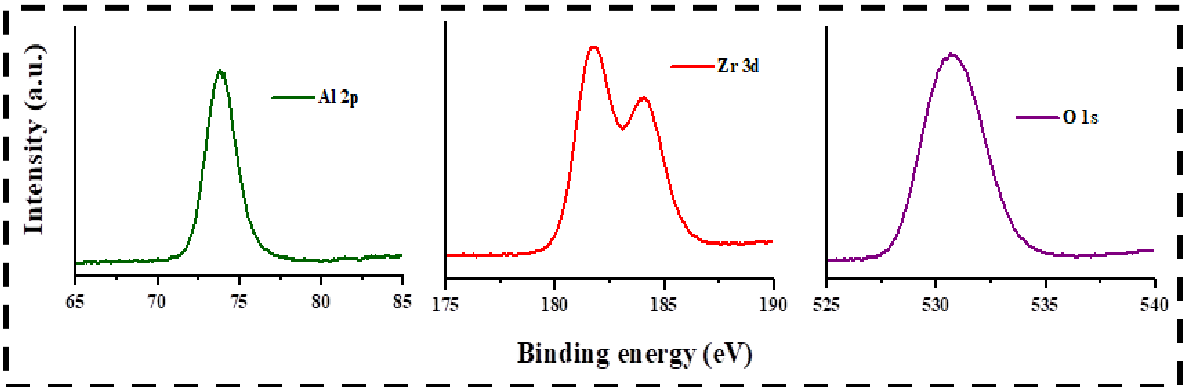


Figure 5: XPS analysis of the synthesized Al_2O_3-ZrO_2 (AlZr) catalyst.

From the figure 5 the Al 2p spectra exhibited clear features at 74.80 and 73.42 eV, indicating a consistent +3 oxidation state for aluminium. Meanwhile, analysis of Zr 3d core level spectroscopy revealed distinct peaks at around 182.0 eV and 184.5 eV for Zr 3d5/2 and Zr 3d3/2, respectively, indicating a +4 oxidation state for zirconium. These findings align with typical values for Zr^{4+} oxidation state in X-ray photoelectron spectroscopy, providing crucial insights into the chemical environment and electronic structure of zirconium in the material.

Furthermore, the O 1s core level analysis unveiled a prominent peak at 530.4 eV, corresponding to oxygen species in the lattice oxygen of the Al_2O_3-ZrO_2 catalysts. This data highlighted the sensitivity of binding energies to the specific metal ions present, with a noticeable shift towards higher values compared to pure Al_2O_3, indicating a strong metal-support interaction. The presence of metal species influenced the chemical environment and energy states of oxygen species within the material.

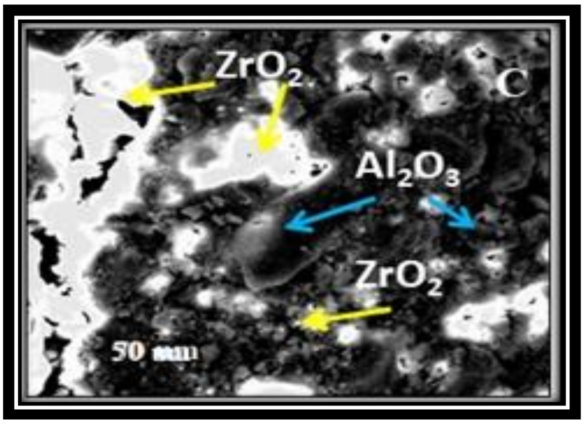


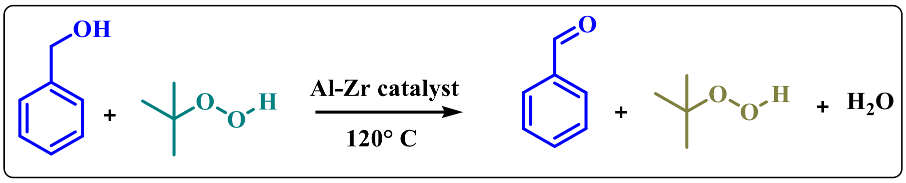
Figure 6: SEM analysis of the synthesized Al_2O_3-ZrO_2 (AlZr) catalyst.

Figure 6 illustrates how the synthesised Al-Zr catalyst's SEM investigation showed unique morphologies for each oxide. Al_2O_3 showed irregular forms with strong agglomeration, whereas ZrO_2 showed regular shapes with little agglomeration. The mixed oxides, on the other hand, showed an almost amorphous structure, which was consistent with the XRD results. Compared to the individual oxides, the combined oxides showed a more homogenous particle structure because ZrO_2 was equally distributed throughout the Al_2O_3 matrix. This demonstrates how ZrO_2 and Al_2O_3 work in concert to potentially improve their applicability for applications that call for a uniform particle dispersion.

4. CATALYTIC ACTIVITY STUDIES

4.1 Catalysts Screening Test

The catalytic oxidation of benzyl alcohol was performed over the Al_2O_3-ZrO_2 (1:1) (Al-Zr) mixed oxide and single metal oxide catalysts under the solvent-free conditions in the batch reactor and obtained results are presented in the scheme 1**.** In every experiment, 13 mmol of benzyl alcohol, 78 mmol of TBHP, 120 °C of reaction temperature, 10 wt.% of catalyst with respect to benzyl alcohol, 14 h of reaction time and 800 rpm of stirring speed. Form the Fig. 5, the pure Al_2O_3 and ZrO_2 individual metal oxide catalysts showed lower conversion of benzyl alcohol (56.3 and 52.0%) with selective toward the benzaldehyde (55.0 and 57.9%) product, respectively. The Al_2O_3-ZrO_2(1:1) mixed oxide catalyst showed a higher conversion (71%) of benzyl alcohol and selectivity towards the benzaldehyde (85%) product in comparison to that of individual metal oxide catalysts. Among all the Al_2O_3-ZrO_2mixed oxide catalysts, the Al_2O_3-ZrO_2 catalyst exhibited superior catalytic efficiency for this transformation, is due to the greater specific surface area, composition of Al_2O_3-$ZrO_2$and higher strength along with large number of active sites (Figure 6).



Scheme 1: Catalytic oxidation of benzyl alcohol

$$\text{Conversion (\%)} = \frac{n_R^{t=0} - n_R^{t}}{n_R^{t=0}} \times 100$$

$$\text{Selectivity (\%)} = \frac{n_i^{t}}{n_R^{t=0} - n_R^{t}} \times 100$$

Where ,

$n_i^t \rightarrow moles\ of\ product\ "i"formed$

$n_R^{t=0} \rightarrow initial\ moles\ of\ reactant\ "R"$

$n_R^t \rightarrow final\ moles\ of\ reactamt\ "R"$

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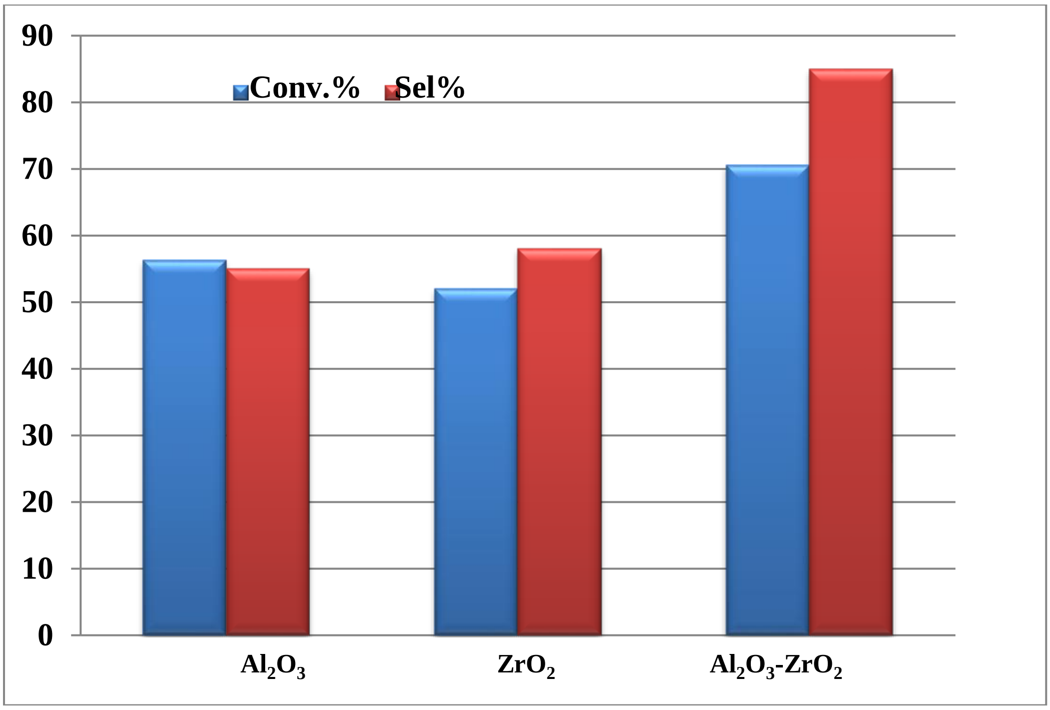


Figure 6: Catalytic oxidation of BOL using TBHP over Al_2O_3, ZrO_2 and mixed oxide

4.2 Effect of Reaction Temperature

The reaction temperature plays a crucial role in catalytic reactions, significantly affecting the rate constants. The impact of temperature on the oxidation of BOL was studied at temperatures ranging from 60° C to 160° C using an Al-Zr catalyst, with other conditions kept constant (Figure 7). The conversion of BOL showed an increasing trend with rising temperature. As the temperature increased, the BOL conversion improved from approximately 27% to about 93%. At 60° C, we observed around 27% conversion and 96% selectivity. The highest selectivity for BOL was achieved at 120° C, with a conversion rate of 94.5%. However, further increasing the temperature to 160° C resulted in a conversion rate of 93%, but the selectivity dropped to 70%, likely due to the over-oxidation of BOL to by-products like benzoic acid. Therefore, 120°C was determined to be the optimal reaction temperature, yielding the maximum amount of the desired product for the oxidation reaction.

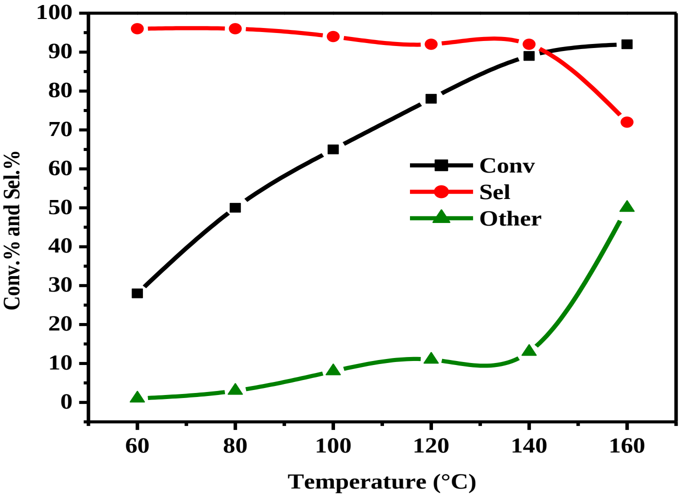


Figure 7: Temperature effect on catalytic oxidation of BOL using TBHP

4.3 Effect of Reaction Time

Reaction time is another crucial parameter in the oxidation of BOL that enhances the yield of BAL. The reaction times ranged from 2 to 16 hours, and the results are shown in Figure 8. At 2 hours, the BOL conversion rate was 10.3% with a selectivity of 98%. As the reaction time increased to 14 hours, the conversion rate significantly improved. However, extending the reaction time beyond 14 hours resulted in a decrease in selectivity to 75.2%. This decline is likely due to the over-oxidation of BAL in the presence of TBHP, leading to the formation of by-products. Therefore, 14 hours was identified as the optimal reaction time for selectively producing BAL.

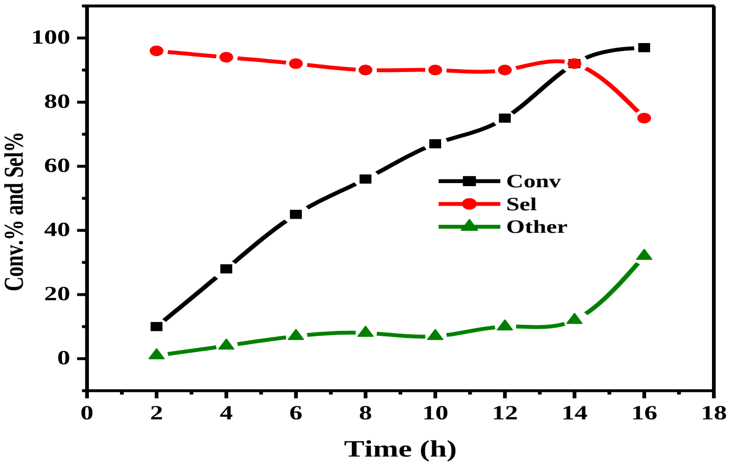


Figure 8: Time factor study on catalytic oxidation of BOL using TBHP

4.4 Effect of Catalyst Loading

The effect of catalyst loading on the catalytic oxidation of BOL to BAL was examined (Figure 9). The reactions were performed using a high-performance Al-Zr mixed oxide catalyst at 120°C, with a 1:6 molar ratio of BOL to TBHP, a reaction time of 14 hours, and a stirring speed of 800 rpm. As the catalyst loading increased from 75 mg to 150 mg, the conversion improved from 40% to 94.5%, while the selectivity decreased from 98.1% to 91.3%. Further increasing the catalyst weight reduced selectivity to 75.1%. This indicates an increase in the number of catalytically active sites on the catalyst surface. It suggests that higher catalyst loading enhances the residence time of BOL on the catalyst surface, leading to over-oxidation to by-products and reduced BAL selectivity. Therefore, a catalyst loading of 150 mg, achieving 94.5% conversion and 91.3% selectivity, was identified as the optimal choice for this reaction.

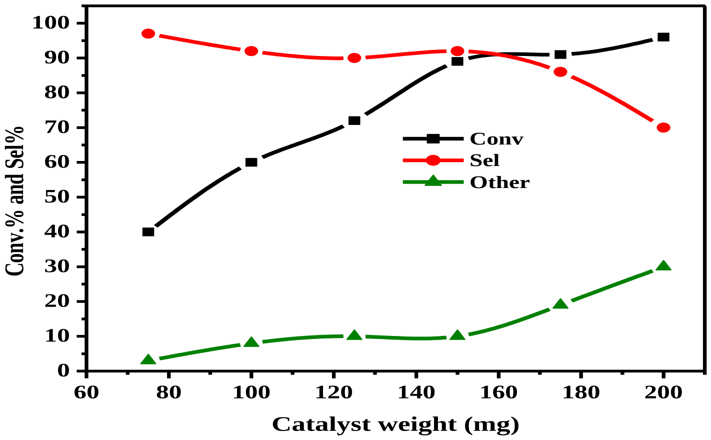


Figure 10: Catalyst loading effect on catalytic oxidation of BOL using TBHP

4.5 Reusability

To assess the robustness and recyclability of the catalyst, we conducted the selective oxidation of BOL using the high-performance Al-Zr catalyst over five cycles under optimized reaction conditions. The results, shown in Figure 11, indicate that the Al-Zr catalyst can be reused for up to five catalytic runs. After each run, the heterogeneous Al-Zr catalyst was recovered, washed several times with methanol to remove any substrate or product residues from its surface, and then pre-activated at 423 K for 2 hours in a hot air oven. As depicted in Fig. , there was no significant decrease in BOL conversion and BAL selectivity up to the fourth cycle. However, in the fifth cycle, the catalytic efficiency of the Al-Zr catalyst decreased substantially, resulting in a BAL conversion rate of 66.3%. This reduction in efficiency is likely due to the deactivation of the Al-Zr catalyst after the fourth cycle.

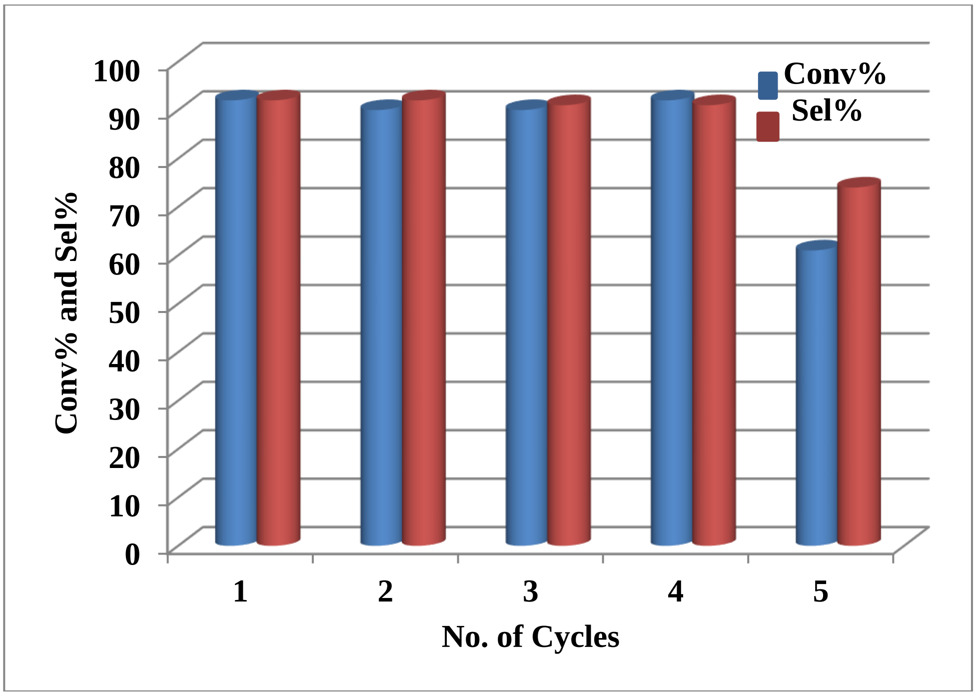
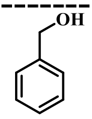
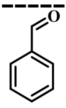


Figure 11: Reusability study on catalytic oxidation of BOL using TBHP

4.6 Substrate scope study

To study the catalyst's substrate broadness and broader applicability, a range of structurally varied aromatic primary and secondary alcohols were oxidized using a high-performance Al-Zr catalyst under optimized reaction conditions. The oxidation was catalyzed by TBHP and involved alcohols with different substituents such as -CH_3, -OCH_3, -OH, -NO_2, and -BR. The results in Table 2 clearly illustrate that differing substituents (both electron-withdrawing and electron-donating groups) had a substantial impact on the products' conversion and selectivity.

Table 2: Substrate scope study on catalytic oxidation of BOL using TBHP

SN	Reactant	Product	Conv.%	Sel.%
1			89	92

ISSN:1624-1940
DOI 10.6084/m9.figshare.26075233
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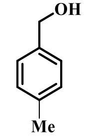
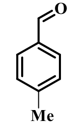
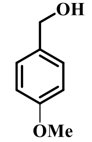
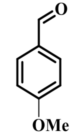
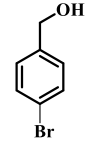
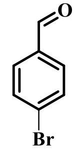
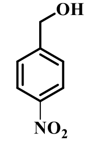
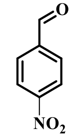
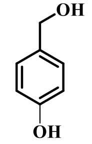
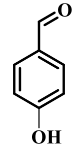
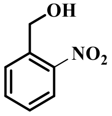
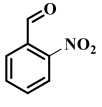
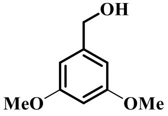
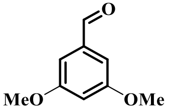
2			90	95
3			89	95
4			74	82
5			65	80
6			67	86
7			58	88
8			77	90

5. CONCLUSIONS

The Al-Zr binary metal oxides showed excellent catalytic activity in the solvent-free oxidation of benzyl alcohol (BOL) to benzaldehyde (BAL), with good selectivity. The Al-Zr catalyst obtained a phenomenal BOL conversion rate of roughly 94% and a BAL selectivity of around 91%. This remarkable catalytic efficiency is due to the catalyst's bigger specific surface area, smaller particle size, increased strength, and abundance of active sites. The basic sites were critical in deprotonating the alcohol and activating the C-H bond on the neighboring α-carbon of the alcohol. The catalyst also demonstrated great stability, with its efficiency remaining constant after four rounds of recyclability trials.

FUNDING: The authors acknowledge the support from TSCOST project (Lr.No.03/TSCOST/DST-PRG/2021-22).

CONFLICT OF INTEREST: There is no conflict of interest.

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ISSN:1624-1940
DOI 10.6084/m9.figshare.26075233
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